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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of:      Edouard A. Mamedov  
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Serial No.:    10/036,866                      Group Art Unit:    1626

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For:    Catalyst Compositions for the Ammoxidation of Alkanes and  
Olefins, Methods of Making and of Using Same

Mail Stop Non-Fee Amendment  
Commissioner for Patents  
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DECLARATION UNDER 37 CFR §1.132

Edouard A. Mamedov, says that:

I am a research scientist and team leader for SABIC Technology Center, SABIC Americas, Inc. My educational background is as follows: I hold a degree of a Bachelor of Science in Chemistry from Baku State University received in 1964 and a degree of a Doctor of Philosophy in Chemistry from the Institute of Catalysis received in 1971.

My duties involve research in the field of propane ammoxidation to acrylonitrile, including catalysts such as those disclosed in U.S. patent no. 5,008,427. I have worked in the

field of ammoxidation catalysis for over twenty-five years, specializing in propane ammoxidation to acrylonitrile for the last four years. I am the author or co-author of seventeen articles and one book on alkylaromatics ammoxidation and have approximately three U.S. patents naming me as an inventor or co-inventor in this field. In view of my qualifications as specified above, I consider myself to be an expert in the art of ammoxidation catalysis, and specifically, propane ammoxidation to acrylonitrile.

I have read the above-identified patent application and the Office Action dated July 2, 2003, including the cited reference U.S. Patent no. 5,008,427.

Under my supervision, the following laboratory experiments were carried out. The first example below was a duplication of Example 6 of the present patent application having a nominal composition  $\text{VSb}_9\text{Ti}_6\text{O}_x$ :

Under vigorous stirring, 8.68 g  $\text{TiCl}_4$  was added in 300 mL of de-ionized water at room temperature via dropping funnel. An exothermic reaction occurred, and a white precipitate was formed. After addition of  $\text{TiCl}_4$ , pH was adjusted to 9.0 with 30%  $\text{NH}_4\text{OH}$  to obtain white slurry. 15.4 g  $\text{SbCl}_3$  was dissolved in 30 mL diluted nitric acid with a  $\text{HNO}_3$  to  $\text{H}_2\text{O}$  volume ratio of 1:3 to obtain syrupy slurry. This slurry was added to the

pale-yellow solution of 0.877 g  $\text{NH}_4\text{VO}_3$  in 50 mL of de-ionized water at  $90^\circ\text{C}$ . The heat under the suspension was turned off, and the slurry was stirred for 30 minutes. The pH of the greenish-white slurry was adjusted to 8.5 with 30%  $\text{NH}_4\text{OH}$ . This alkaline slurry was then added to the above-prepared slurry of  $\text{TiCl}_4$  and stirred for an hour. The precipitate was filtered and transferred to a porcelain dish, dried and calcined in air under the following ramp conditions: room temperature to  $120^\circ\text{C}$  at  $5^\circ\text{C}/\text{min}$ , held for 5 hours;  $430^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$ , held for 4 hours;  $650^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$ , held for 6.5 hours. The calcined material was cooled down to room temperature, ground to fine powder, pressed and sieved to 18-30 mesh.

The second example below was a duplication of Example M of U.S. Patent no. 5,008,427 having an empirical composition  $\text{VSbTi}_{6.75}\text{O}_x$ :

27.58 g of  $\text{V}_2\text{O}_5$  powder was slurried in 400 cc of water in a 1.0 liter beaker. While vigorously stirring, 70 g of a 30%  $\text{H}_2\text{O}_2$  solution in water was slowly added and the  $\text{V}_2\text{O}_5$  began to dissolve. In this step the peroxovanadium ion forms. After about 15 minutes some undissolved  $\text{V}_2\text{O}_5$  remained, and another 70 g of the 30%  $\text{H}_2\text{O}_2$  solution was added with continued stirring. The

final dispersion was a red solution with some orange flocculent solids.

44.2 g of powdered  $\text{Sb}_2\text{O}_3$  was added to the foregoing dispersion. The mixture was stirred for about 4 hours with heating in order to reduce the volume by evaporation of water. During this time, the slurry formed gradually, turned to a deep blue-green, then finally to a blackish green. The additional element Ti was introduced as a  $\text{TiO}_2$  sol. 164 g of  $\text{TiO}_2$  was added in the slurry resulting from the reaction of the vanadium compound and the antimony compound. When the mixture could no longer be stirred, it was dried in an oven for about 16 hours at  $100^\circ\text{C}$ . Thereafter, it was calcined for 8 hours at  $650^\circ\text{C}$ ., cooled and then crushed and sieved to 20-35 mesh. The calcined material was very hard.

A portion of this catalyst was activated by calcining for 1 hour at  $950^\circ\text{C}$ . A portion of the activated catalyst was washed with water in a Soxhlet extractor for several hours until the wash water appeared colorless. The washed catalyst was then dried by heating at about  $100^\circ\text{C}$ . for about 3 hours.

Both samples were analyzed by powder X-ray diffraction (XRD) on the same instrument. As is seen from Table 1 and attached XRD patterns, the reference catalyst contained rutile-type  $\text{VSbO}_4$  phase which indicates that vanadium and antimony sites are not isolated in a matrix of metal oxides. The claimed catalyst does not contain  $\text{VSbO}_4$ . The distinctive peaks designated by "x" in the attached XRD patterns are not present in the claimed catalyst. These XRD results demonstrate that the claimed catalyst has a different composition from that of the reference catalyst in that the vanadium and antimony sites are isolated in a matrix of metal oxides.

Both catalyst samples were tested for propane ammoxidation to acrylonitrile under the same conditions. The results of this comparative study are presented in Table 1.

**Table 1**

Catalyst formulation	Preparation method	Phases	$\tau^1$ (s)	$T^2$ ( $^{\circ}\text{C}$ )	Propane <sup>3</sup> Conv. (%)	ACN Sel. (%) <sup>4</sup>
$\text{VSbTi}_{5.75}\text{O}_x$	5,008,427 Example M	$\text{TiO}_2$ , $\text{VSbO}_4$	0.3	475 500	6.7 9.7	14.0 21.3
			0.5	475 500	14.9 18.5	19.6 25.8
$\text{VSb}_9\text{Ti}_6\text{O}_x$	10/036,866 Example 6	$\text{TiO}_2$ , $\text{Sb}_2\text{O}_3$	0.5	475 500	9.6 11.4	48.2 51.0
			2.0	475 500	13.8 17.7	48.5 48.0

- <sup>1</sup> Contact time, seconds
- <sup>2</sup> Reaction temperature, degrees Celsius
- <sup>3</sup> Feed  $C_3H_8/NH_3/O_2/He = 18/8/15/59$ , volume %
- <sup>4</sup> Acrylonitrile selectivity based on propane

Product selectivity in oxidation reactions is related to hydrocarbon conversion. To reduce this effect, the selectivities of different catalysts are usually compared at similar conversions. Under the conditions listed in Table 1, the reference catalyst gave 19.6% selectivity to acrylonitrile at propane conversion 14.9% for a contact time of 0.5 sec and at a temperature of 475°C. Comparison of reference catalyst with the claimed catalyst shows that the latter is more selective with respect to acrylonitrile production. For instance, the claimed catalyst displayed 48.2% selectivity to acrylonitrile at conversion 9.6% at the same process conditions. For a contact time of 0.5 sec and at a temperature of 500°C, the reference catalyst gave 25.8% selectivity at 18.5% conversion compared to 51.0% selectivity at 11.4% conversion for the claimed catalyst. It is believed that this significant difference in acrylonitrile selectivity is related to the structural differences of the catalysts as confirmed by the XRD results discussed above.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made herein on information and belief are believed to be true; and further that all statements herein were made with the knowledge that willful false statements and the like so made are punishable by fine or

SERIAL NO. 10/036,866

PATENT APPLICATION

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imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

*E. Mamedov*

Signature

8/28/03

Date